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PREPARATION METHOD FOR ANALYZING
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Author(s):

Christopher G. Worley

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QUANTIFICATION OF GALLIUM IN DRIED RESIDUE SAMPLES BY XRF: AN IMPROVED SAMPLE PREPARATION METHOD FOR ANALYZING PLUTONIUM METAL

Christopher G. Worley

Los Alamos National Laboratory, MS G740, Los Alamos, NM 87545

ABSTRACT

A novel XRF sample preparation method was investigated to quantify the concentration of gallium in plutonium metal and minimize the possibility of contaminating the instrument with radioactive material. To prepare homogenous specimens and to add an internal standard, the plutonium must first be dissolved. The currently established method then entails removing the plutonium by chromatography and analyzing the gallium remaining in solution. In the work presented here, plutonium solution aliquots containing zinc as an internal standard were cast onto Mylar, dried, and analyzed by XRF. Aqueous standards containing gallium and zinc were first cast as dried residues, and these residue standards were analyzed and calibrated. More recently aqueous standards containing plutonium, gallium, and zinc were prepared, cast as dried spots, and calibrated. Very linear calibrations were obtained for both sets of standards when zinc was used as the internal standard (RMS values $\leq 1\%$ of the standards concentration range). Hence, this dried residue process appears very promising for quantifying gallium in plutonium metal.

INTRODUCTION

Determining the concentration of gallium in plutonium metal is vital in manufacturing nuclear weapons, and wavelength-dispersive XRF is a key method used to quantify the gallium due to its good precision and accuracy using matrix-matched standards. The established XRF sample preparation method currently used involves dissolving the plutonium to prepare a homogenous specimen and employing ion exchange chromatography to remove the plutonium prior to analysis for gallium.[1] This is performed to minimize the amount of plutonium introduced into the instrument. However, some residual plutonium and trace levels of americium are present in the solution after the ion exchange process which results in a radioactive liquid specimen. Therefore, the potential exists for the XRF specimen cup film to rupture during analysis resulting in leakage of radioactive liquid. In addition, the ion exchange process and subsequent preparation steps take at least two days to complete, and considerable aqueous radioactive waste is generated which is expensive to discard. Hence, an improved method for sample preparation is desirable.

Casting solutions as dried residues for XRF analysis has been investigated in the past for preconcentrating trace elements to improve the detection limits.[2-6] In the present study, dried residue specimens were cast from solution to produce dry specimens and eliminate the possibility of radioactive solution leaking into the spectrometer. This sample preparation method can also be performed in a few hours as opposed to the two days necessary with the aqueous ion exchange method, and considerably less radioactive waste is generated as well.

In previously reported work, aqueous gallium standards were prepared, cast as dried residue standards, analyzed, and calibrated.[7] In the current report, the calibration from these standards will be reviewed, and new data will be presented in which plutonium-containing standards were cast as dried residue specimens and calibrated.

EXPERIMENTAL

Instrument. A Philips Analytical PW2404 wavelength-dispersive XRF spectrometer with a 4000 W rhodium anode was used. The data were collected under helium. A LiF detector crystal and a 300 μm detector collimator were employed. Both the gallium and zinc intensities were collected using 50 kV and 60 mA. A 2Θ angle of 38.9° was used to collect the gallium count rate ($K\alpha$ line), and a 2Θ angle of 41.8° was used for the zinc count rate ($K\alpha$ line).

Non-radioactive standards calibration. The gallium channel analysis time was 36 sec, and two background channels at 38.3° and 39.4° were collected for 12 sec each. The zinc channel analysis time was 36 sec, and two background channels at 41.1° and 42.3° were acquired for 12 sec each.

Plutonium-containing standards calibration. A gallium channel analysis time of 208 sec was used. Significant absorption by the plutonium resulted in poor signal-to-noise (S/N) at short counting times. Therefore, the necessary counting time was significantly longer than that for the non-radioactive standards in order to achieve adequate S/N. Two gallium background channels at 38.4° and 39.4° were acquired for 104 sec and 94 sec respectively. The zinc channel was collected for 124 sec, and two background channels at 41.3° and 42.3° were acquired for 44 and 40 sec respectively.

Standards. Non-radioactive standards. The following standards were prepared using 0.5 M HNO_3 as the solvent: 0, 50, 100, 250, 500, 750, 1000, 1250, and 1500 ppm gallium. A 10 mg/mL gallium NIST traceable standard (High Purity Standards) was used to prepare the above secondary standards. Zinc was added at 1000 ppm to serve as an internal standard using a 10 mg/mL zinc NIST traceable standard (High Purity Standards). A 6 μm thick Mylar film (Somar International) was mounted on a double open ended specimen cup (Chemplex Industries), and seven 15 μL drops of the standard solution were cast on the cell interior side of the film in a face-centered hexagonal arrangement. This was repeated for each standard. The drops were air dried for 30 min using a heat lamp placed ~ 25 cm above the cells, and the open end of the cells were then capped with microporous Teflon film for analysis. A 3.6 μm thick Mylar film (Somar International) was used as secondary containment and placed over the primary 6 μm film. These standards were then analyzed and calibrated.

Plutonium-containing standards. The same materials vendors used for the non-radioactive standards were also used here (standard stock solutions, XRF film, etc.). The standards were prepared using gallium masses rather than concentrations and consisted of the following masses: 0, 100, 300, 700, 1000, 1300, 1700, and 2000 μg of gallium. To serve as an internal standard, 2000 μg of zinc were added to each standard. Inside an open-front box, 0.17 g of high purity electrorefined plutonium was added to each standard, and 0.5 M HNO_3 was added to bring the total volume up to 10 mL. A 6 μm Mylar film was mounted on a double open ended specimen cup, and seven 15 μL drops of the standard solution were cast on the cell interior side of the film

in a face-centered hexagonal pattern. This was repeated for each standard, and two such specimens were prepared from each standard solution. The drops were air dried for 45 min inside the open-front box, using a heat lamp placed ~25 cm above the cells, and the open end of each cell was then sealed with microporous Teflon film. Using an α radiation monitor, each cell was verified to be free of any external contamination, and 3.6 μm Mylar film was placed over the primary 6 μm film to act as secondary containment during the analysis.

RESULTS AND DISCUSSION

The method of dissolving plutonium metal, removing the plutonium, and analyzing the remaining gallium in solution by XRF is well established in our laboratory and produces good precision and accuracy. A precision RSD of 0.33% was measured for 6 plutonium samples, and the average gallium concentration value deviated by 0.81% from the known value determined by isotope dilution mass spectrometry. Further, a very linear calibration curve was prepared from aqueous gallium standards with an RSD of 0.05% of the standards concentration range (see table 1).

| Type of Standard | RMS (% of concentration range) |
|--|--------------------------------|
| Aqueous with Zn internal standard | 0.05 |
| Ga dried residue with Zn internal standard | 0.3 |
| Pu, Ga, and Zn dried residue – No Zn ratio | 9.6 |
| Pu, Ga, and Zn dried residue – With Zn ratio | 1.0 |
| Pu, Ga, and Zn dried residue – Omission of flyer | 0.6 |

Table 1. Calibration linearity for different standards types.

Non-radioactive dried residue standards. In preliminary work previously reported, dried residue standards containing gallium and zinc were prepared by casting them as dried spots. They were then analyzed by XRF and calibrated.[7] While these standards did not contain plutonium, the calibration did demonstrate the potential for casting specimens as dried spots and quantifying the gallium content. An RMS of 0.3% of the standards concentration range was achieved (table 1). Although this linear fit is not as tight as that obtained from the aqueous standards (0.05%), it is nevertheless impressive for the calibration of dried residue specimens.

Plutonium-containing dried residue standards. Since the specimen spots cast from the plutonium/gallium/zinc standard solutions consisted primarily of plutonium nitrate (cast from 0.5 M HNO_3 solution), the gallium signal was substantially attenuated due to absorption by the plutonium. Hence, the use of zinc as an internal standard was essential to account for this pronounced matrix effect and reduce the precision to an acceptable level. The gallium calibration of these plutonium-containing standards without using the gallium/zinc intensity ratio is depicted in figure 1. Clearly there is a great deal of variance in the data. (Note that two specimens were prepared from each of the eight standard solutions, and both are included in the calibration, whereas only one specimen per standard was used in the previous non-radioactive standards calibration as well as in the aqueous standards calibration.) When the gallium/zinc intensity ratio was used instead of the gallium intensity alone, the calibration linearity increased markedly with an RMS of 1.0 % of the concentration range (table 1 and figure 2). Therefore, the

zinc minimized the plutonium matrix effect. One of the two 1000 μg gallium standard specimens was determined to be a 2σ data flyer. When this data point was not included in the calibration, the RMS was reduced further to 0.6% of the concentration range (table 1 and figure 3) which is close to the calibration linearity achieved from the dried residue standards that did not contain plutonium.

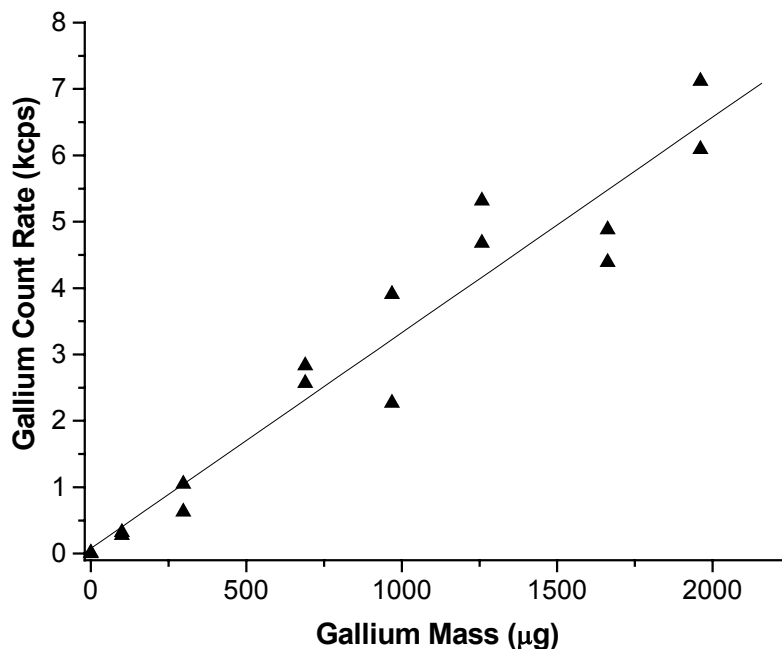


Figure 1. Plutonium-containing dried residue standards calibration without ratioing to the zinc internal standard intensity.

Precision and accuracy. To determine the precision and accuracy using the plutonium-containing dried residue calibration (using the gallium/zinc intensity ratio), five dried residue specimens were prepared from the gallium standard solution containing 1000 μg of gallium, and five specimens were prepared from the standard containing 1300 μg of gallium. The gallium content was then quantified for each of these specimens. The precision (RSD) and accuracy corresponding to each set of five measurements are listed in table 2. The average RSD for both standards was 2.68 %, and the average relative error was 2.74 %. These values are not as low as those achieved using the conventional aqueous method to prepare plutonium samples (RSD = 0.33% and relative error = 0.81% for the measurement of six plutonium samples). However, this level of precision and accuracy is respectable given that the specimen dried residue spots consist primarily of plutonium nitrate which results in marked matrix effects. There is a 0.6 keV energy difference between the gallium and zinc $K\alpha$ lines used for quantification, which likely resulted in a small difference in the absorption of the gallium and zinc X-ray photons by the plutonium.

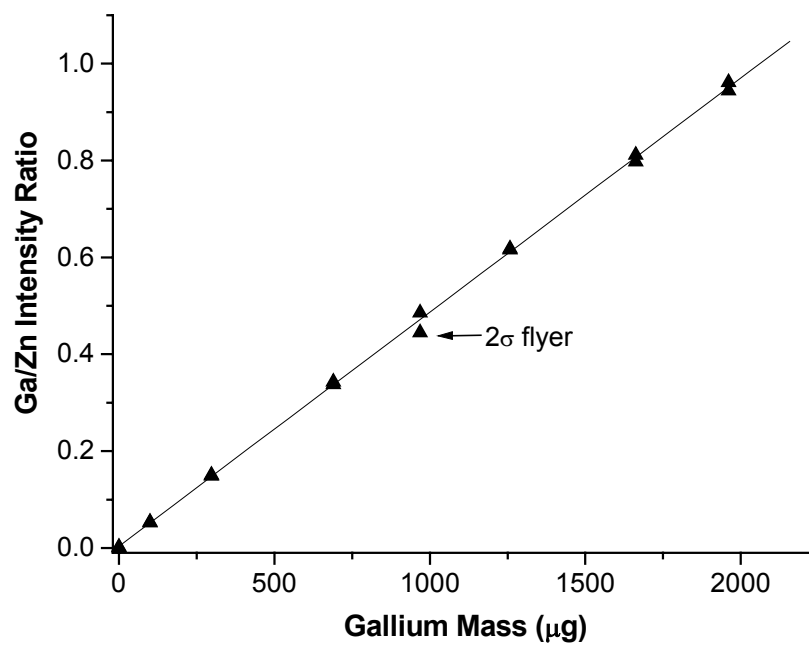


Figure 2. Dried residue standards calibration using the internal standard ratio.

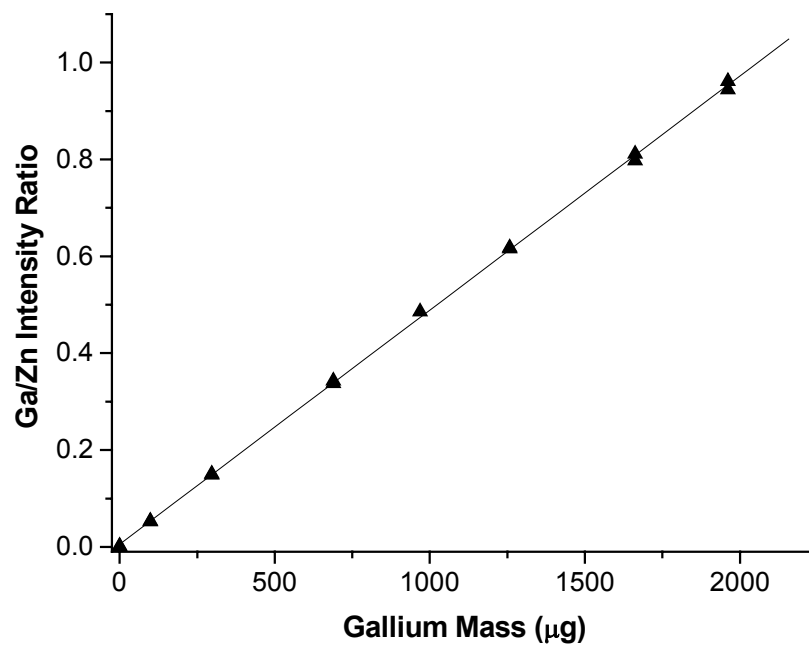


Figure 3. Calibration without including the 2 σ flyer data point.

| Standard | RSD (%) | Relative error (%) |
|-----------------|---------|--------------------|
| 1000 µg gallium | 3.68 | 1.72 |
| 1300 µg gallium | 1.67 | 3.75 |

Table 2. Precision and accuracy measurements from 5 specimens/standard.

CONCLUSIONS

The dried residue sample preparation method was demonstrated to be a feasible means of preparing plutonium samples for gallium quantification by XRF. The method is safer, generates less waste, and is considerably faster than preparing aqueous specimens by the established method currently employed. Linear calibrations were obtained from dried residue standards containing only gallium and zinc and from standards also containing plutonium. Although the presence of plutonium introduces considerable matrix effects, using zinc as an internal standard for the gallium markedly reduces these effects and greatly improves the precision and accuracy. Repeated measurements of two of the plutonium-containing dried residue standards resulted in an average precision RSD of 2.68 % and an average relative error of 2.74 %. While these values are not as low as are possible using the aqueous sample preparation approach, they are certainly adequate for a rapid QA/QC screening method to quantify gallium in plutonium metal.

Future plans for this work include analyzing a series of plutonium samples which have been well characterized by other methods. The accuracy and precision for analyzing real plutonium unknowns will then be determined from these measurements. Investigations are also underway to determine the optimum number of specimens per sample needed to achieve acceptable precision while minimizing the total analysis time. Finally, interelement correction factors between plutonium and gallium and zinc will be examined to determine if the precision and accuracy can be further reduced.

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